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A reexamination of the potential constants of group IV halides

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All the five independent potential constants in thirty cases of tetrahedral group IV halides have been recalculated on the basis of the kinetic constants of these molecules. The results appear to show the basic importance of kinetic constants in molecular dynamics. The need for a proper appraisal and application of the provisions of group theoretical techniques in the study of molecular vibrations in general is also established. Further, the present set of force constants have been utilised to evaluate mean amplitudes of vibration of these molecules and they, again, appear to be reasonable.

1. INTRODUCTION

Wilson's group theoretical method of analysis of molecular vibrations has been of great service in the study of molecular forces (Wilson 1939, 1941). The present paper, relating to the potential constants of the XY_4 tetrahedral group IV halides, adopts wilson's techniques coupled with three simplifying considerations in an advantageous manner. Firstly, it is important to recognise all the internal coordinates in any molecule for constructing symmetry coordinates. In recent studies, regarding the bent symmetrical XY_2 molecules and the pyramidal XY_3 molecules (Thirugnanasambandam & Mohan 1974a, 1975a) a new set of internal coordinates relating to reflex angles has been recognised, in addition to the usual internal coordinates. Extending this procedure to the molecular type under consideration, six more internal coordinates have been introduced for the first time. Hence, a revised set of symmetry coordinates has been employed in the present investigation. Secondly, it is necessary to distinguish between independent and non-independent force constants in any molecule. The most general quadratic potential energy function consists of fifteen force constants in this type of molecules. Out of these fifeen force constants, ten are non-independent. The redundant symmetry coordinates give rise to redundancy constraints which provide links between non-independent force constants and some of the independent force constants. Thus these links are useful to elimenate the non-independent force constants. Hence, one is left with just the independent force constants to be evaluated

from the spectral frequencies in these molecules. Thirdly the kinetic constants of molecules appear to be of basic significance in the study of molecular vibrations. They have been advantageously employed in different cases (Thirugnanasambandam *et al* 1959, 1974a, 1974b, 1975a, 1975b, 1976a, 1976b) to obtain acceptable sets of force constants in polyatomic molecules in a simple manner. This elegant procedure has been extended here to evaluate all the independent potential constants of group IV halides belonging to tetrahedral XY_4 structure. Further, the force constants obtained here, are utilised to evaluate the mean amplitudes of the thirty molecules under consideration. The results are again equally interesting and they appear to be reasonable. Thus it appears that the kinetic constants play major roles in the molecular architecture and effectively participate in molecular dynamics.

2.1. Theoretical Considerations

The tetrahedral XY_4 molecule consists of four bonds, the usual six inter-bond angles and the newly-introduced six angles which are reflex angles to the six interbond angles. Thus all the sixteen internal coordinates have been used in constructing sixteen symmetry coordinates satisfying the usual conditions. The tetrahedral XY_4 structure belongs to the T_d point group and gives rise to one non-degenerate vibration of A_1 type, one doubly degenerate vibration of E type and two triply degenerate vibrations of F_2 type.

2.2. Symmetry Coordinates

A_1 TYPE:

$$S_1 = (1/\sqrt{4})\,(\Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4)$$

$$S_{r_1} = (1/\sqrt{12})\,(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\alpha_{41} + \Delta\alpha_{42} + \Delta\alpha_{43} + \Delta\beta_{12} + \Delta\beta_{23} + \Delta\beta_{31} + \Delta\beta_{42} + \Delta\beta_{43} + \Delta\beta_{13}) = 0 \text{ (Redundant)}$$

$$S_{r_2} = (1/\sqrt{12})\,(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\alpha_{41} + \Delta\alpha_{42} + \Delta\alpha_{43} - \Delta\beta_{12} - \Delta\beta_{23} - \Delta\beta_{31} - \Delta\beta_{41} - \Delta\beta_{42} - \Delta\beta_{43}) = 0 \text{ (Redundant)}$$

E TYPE:

$$S_{2a} = (1/\sqrt{24})\,(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{41} - \Delta\alpha_{42} + 2\Delta\alpha_{43} - 2\Delta\beta_{12} + \Delta\beta_{23} + \Delta\beta_{31} + \Delta\beta_{41} + \Delta\beta_{42} - 2\Delta\beta_{43})$$

$$S_{2b} = (1/\sqrt{8})\,(\Delta\alpha_{41} - \Delta\alpha_{31} - \Delta\alpha_{23} - \Delta\alpha_{42} - \Delta\beta_{41} + \Delta\beta_{31} + \Delta\beta_{23} + \Delta\beta_{42})$$

$$S_{r_3} = (1/\sqrt{24})\,(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{41} - \Delta\alpha_{42} + 2\Delta\alpha_{43} + 2\Delta\beta_{12} - \Delta\beta_{23} - \Delta\beta_{31} - \Delta\beta_{41} - \Delta\beta_{42} + 2\Delta\beta_{43}) \equiv 0 \text{ (Redundant)}$$

$$S_{r_4} = (1/\sqrt{8})\,(\Delta\alpha_{41} - \Delta\alpha_{31} + \Delta\alpha_{23} - \Delta\alpha_{42} + \Delta\beta_{41} - \Delta\beta_{31} + \Delta\beta_{23} - \Delta\beta_{42}) \equiv 0 \text{ (Redundant)}$$

F_2 TYPE:

$$S_{3a} = (1/\sqrt{6})\ (\Delta d_1+\Delta d_2-2\Delta d_3)$$

$$S_{3b} = (1/\sqrt{12})\ (\Delta d_1+\Delta d_2+\Delta d_3-3\Delta d_4)$$

$$S_{3c} = (1/\sqrt{2})\ (\Delta d_2-\Delta d_1)$$

$$S_{4a} = (1/\sqrt{24})\ (2\Delta\alpha_{12}-\Delta\alpha_{23}-\Delta\alpha_{31}+\Delta\alpha_{41}+\Delta\alpha_{42}-2\Delta\alpha_{43} -2\Delta\beta_{12}+\Delta\beta_{23}+\Delta\beta_{31}-\Delta\beta_{41}-\Delta\beta_{12}+2\Delta\beta_{43})$$

$$S_{4b} = (1/\sqrt{12})\ (\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}-\Delta\alpha_{41}-\Delta\alpha_{42}-\Delta\alpha_{43} -\Delta\beta_{12}-\Delta\beta_{23}-\Delta\beta_{31}+\Delta\beta_{41}+\Delta\beta_{12}+\Delta\beta_{43})$$

$$S_{4c} = (1/\sqrt{8})\ (\Delta\alpha_{23}-\Delta\alpha_{31}-\Delta\alpha_{41}+\Delta\alpha_{42} -\Delta\beta_{23}+\Delta\beta_{31}+\Delta\beta_{41}-\Delta\beta_{42})$$

$$Sr_5 = (1/\sqrt{24})\ (2\Delta\alpha_{12}-\Delta\alpha_{23}-\Delta\alpha_{31}+\Delta\alpha_{41}+\Delta\alpha_{42}-2\Delta\alpha_{43} +2\Delta\beta_{12}-\Delta\beta_{23}-\Delta\beta_{31}+\Delta\beta_{41}+\Delta\beta_{12}-2\Delta\beta_{43}) \equiv 0 \text{ (Redundant)}$$

$$Sr_6 = (1/\sqrt{12})\ (\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}-\Delta\alpha_{41}-\Delta\alpha_{42}-\Delta\alpha_{43} +\Delta\beta_{12}+\Delta\beta_{23}+\Delta\beta_{31}-\Delta\beta_{41}-\Delta\beta_{42}-\Delta\beta_{43}) \equiv 0 \text{ (Redundant)}$$

$$Sr_7 = (1/\sqrt{8})\ (\Delta\alpha_{23}-\Delta\alpha_{31}-\Delta\alpha_{41}+\Delta\alpha_{42} \Delta\beta_{23}-\Delta\beta_{31}-\Delta\beta_{41}+\Delta\beta_{42}) \equiv 0 \text{ (Redundant)}$$

2.3. Redundancy Constrants and F Matrix

The seven redundant symmetry coordinates give rise to ten redundancy constraints :

$$f'_{d\alpha} + f''_{d\alpha} = 0$$

$$f'_{d\beta} + f''_{d\beta} = 0$$

$$f_{\alpha} + f'_{\alpha\alpha} + 4\, f''_{\alpha\alpha} = 0$$

$$f_{\beta} + f'_{\beta\beta} + 4\, f''_{\beta\beta} = 0$$

$$f_{\alpha\beta} + f'_{\alpha\beta} + 4\, f''_{\alpha\beta} = 0$$

$$(f_{\alpha} + f'_{\alpha\alpha} - 2f''_{\alpha\alpha}) \quad (f_{\beta} + f'_{\beta\beta} - 2\, f''_{\beta\beta}) = 0$$

$$(f_{\alpha} + f'_{\alpha\alpha} - 2f''_{\alpha\alpha}) + (f_{\beta} + f'_{\beta\beta} - 2f''_{\beta\beta}) + 2(f_{\alpha\beta} + f'_{\alpha\beta} - 2f''_{\alpha\beta}) = 0$$

$$(f'_{d\alpha} - f''_{d\alpha}) + (f'_{d\beta} - f''_{d\beta}) = 0$$

$$(f_{\alpha} - f'_{\alpha\alpha}) - (f_{\beta} - f'_{\beta\beta}) = 0$$

$$(f_{\alpha} + f'_{\alpha\alpha}) + (f_{\beta} - f'_{\beta\beta}) + 2(f_{\alpha\beta} - f'_{\alpha\beta}) = 0$$

These redundancy constraints reduce the number of force constants to five in number. The five independent force constants are f_d, f_{dd}, f_α, $f'_{\alpha\alpha}$ and $f'_{d\alpha}$, where f_d is the stretching force constant, f_{dd} is the bond-bond interaction force constant, f_α is the bending force constnt, $f'_{\alpha\alpha}$ is the force constant relating to the interaction between two interior distant angles and $f'_{d\alpha}$ is the interaction force constant between a bond and the corresponding distant interior angle.

The condensed F matrix elements involving the five independent force constants are the following :

A_1 TYPE:

$$F_{11} = f_d + 3f_{dd}$$

E TYPE:

$$F_{22} = 3d^2 (f_\alpha + f'_{\alpha\alpha})$$

F_2 TYPE :

$$F_{33} = f_d - f_{dd}$$

$$F_{44} = 2d^2 (f_\alpha - f'_{\alpha\alpha})$$

$$F_{34} = -4d\, f'_{d\alpha}$$

2.4 G Matrix

The G matrix elements are obtained as usual and they are given below :

A_1 TYPE:

$$G_{11} = \mu_y$$

E TYPE:

$$G_{22} = 6\, \mu_y/d^2$$

F_2 TYPE:

$$G_{33} = \mu_y + (4/3)\, \mu_x$$

$$G_{44} = (4/d^2)[\mu_y + (8/3)\, \mu_x]$$

$$G_{34} = -(8\sqrt{2}/3d)\, \mu_x$$

2.5. Kinetic Constants

The kinetic constants arising out of the expression $2T = \tilde{\dot{S}}\, G^{-1}\, \dot{S}$ are given below

$$k_{d} = (\mu_{v} + 3\mu_{s})/A\,\mu_{v}$$
$$k_{dd} = \mu_{s}/3A\mu_{v}$$
$$k_{\alpha} = (1/144\,\mu_{s})\ (B/A)$$
$$k'_{\alpha\alpha} = -(1/144\mu_{v})\ (C/A)$$
$$k'_{d\alpha} = \mu_{x}/3\sqrt{2}\ A\mu_{y}$$

where $A = \mu_{y} + 4\mu_{x}$
$B = 13\mu_{v} + 28\mu_{s}$
$C = 5\mu_{v} - 4\mu_{x}$

Further, these independent kinetic constants are related to the some of the dependent kinetic constants, similar to the redundancy constraints.

$$k'_{d\alpha} + k''_{d\alpha} = 0$$

$$k'_{d\beta} + k''_{d\beta} = 0$$

$$k_{\alpha} + k'_{\alpha\alpha} + 4k''_{\alpha\alpha} = 0$$

$$k_{\beta} + k'_{\beta\beta} + 4k''_{\beta\beta} = 0$$

$$k_{\alpha\beta} + k'_{\alpha\beta} + 4k''_{\alpha\beta} = 0$$

$$(k_{\alpha} + k'_{\alpha\alpha} - 2k''_{\alpha\alpha}) - (k_{\beta} + k'_{\beta\beta} - 2k''_{\beta\beta}) = 0$$

$$(k_{\alpha} + k'_{\alpha\alpha} - 2k''_{\alpha\alpha}) + (k_{\beta} + k'_{\beta\beta} - 2k''_{\beta\beta}) + 2(k_{\alpha\beta} + k'_{\alpha\beta} - 2k''_{\alpha\beta}) = 0$$

$$(k'_{d\alpha} - k''_{d\alpha}) - (k'_{d\beta} - k''_{d\beta}) = 0$$

$$(k_{\alpha} - k'_{\alpha\alpha}) - (k_{\beta} - k'_{\beta\beta}) = 0$$

$$(k_{\alpha} - k'_{\alpha\alpha}) + (k_{\beta} - k'_{\beta\beta}) + 2(k_{\alpha\beta} - k'_{\alpha\beta}) = 0$$

2.6. Potential Constants

The determination of symmetry force constants, involved in the secular equation, from the n_i vibrational frequencies alone has been a mathematically underdetermined problem so far. Therefore any genuine attempt to evaluate all the symmetry force constants associated with a problem of order $n>1$ should involved the incorporation of atleast n_i $(n_i - 1)/2$ additional data other than the n_i frequencies. The procedure of kinetic constants (Thirugnanasambandam *et al* 1969, 1974-b 1975a-d, 1976a-b) provides the required number of additional data through the symmetry kinetic constants and the corresponding symmetry force constants.

For example, in the 2×2 case, this new procedure gives a constraint-relation governing F_{34} and F_{44} :

$$F_{34}/F_{44} = K_{34}/K_{44}$$

Thus the equations involved in the F_2 species are easily solved.

2.7. Mean Amplitudes

Cyvin's procedure (Cyvin 1968) is adopted here, in evaluating the mean amplitudes of vibration of these molecules, using the present set of force constants.

3. Results and Discussion

Results relating to thirty tetrahedral XY_4 group IV halides are discussed here. The structural parameters and the vibrational frequencies of the molecules studied in the present investigation are given in Table 1. Table 2 gives the kinetic constants of these molecules. The evaluated individual force constant of these molecules are presented in Table 3. Table 4 deals with the force constants in related molecules. The mean amplitudes evaluated here are repored in Table 5.

3.1. *Kinetic Constants :*

The kinetic constants given in Table 2 may be grouped under three heads. viz.,

1. *Bond-angle interactions* group
2. *Bending and angle-angle interactions* group
3. *Stretching and bond-bond interactions* group

Table 1. Structural parameters and vibrational frequencies

S.No.	Molecule	d Å	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$ cm^{-1}	$\nu_4(F_2)$	Ref.
1.	CF_4	1.317	908.5	435	1283	631.2	a, b
2.	SiF_4	1.55	800	268	1031	391	c, d
3.	TiF_4	1.73	704	192	804	232	e
4.	GeF_4	1.67	738	205	800	260	f, g
5.	ZrF_4	2.10	630	160	668	190	e
6.	PbF_4	2.08	564	158	570	180	h, i
7.	CCl_4	1.766	558.7	217	778	313.5	c, j, k
8.	$SiCl_4$	2.02	424	150	610	221	d, k, l
9.	$TiCl_4$	2 180	385	120	496	144	l
10.	$GeCl_4$	2.08	397	147	463	172	m
11.	$ZrCl_4$	2 33	382	108	423	114	l
12.	$SnCl_4$	2.31	368	100	394	131	m
13.	$HfCl_4$	2.41	347	88	378	93	h
14.	$PbCl_4$	2.43	327	90	348	93	i, l
15.	CBr_4	1.942	267	122	671	182	c, j, k
16.	$SiBr_4$	2.15	249	90	487	137	d, k
17.	$TiBr_4$	2.31	230	74	383	91	c, n
18.	$GeBr_4$	2.29	234	78	328	111	g, o
19.	$ZrBr_4$		224	65	309	78	g
20.	$SnBr_4$	2.44	220	64	279	88	c, p
21.	$HfBr_4$	2.56	205	54	240	60	h
22.	$PbBr_4$	2.54	207	59	231	73	h, i
23.	CI_4	2.15	178	90	555	123	k, q
24.	SiI_4	2.43	168	63	405	94	k, d
25.	TiI_4	2.57	155	57	225	100	e
26.	GeI_4	2.50	159	60	264	80	c, r
27.	ZrI_4		152	44	211	55	g
28.	SnI_4	2.64	149	47	216	63	c, r
29.	HfI_4	2.75	142	39	185	46	h
30	PbI_4	2.77	137	37	168	48	h, i

a. Monostori & Weber (1960)
b. Hoffman & Livingston (1953)
c. Sutton (1958)
d. Radhakrishnan (1962)
e. Nagarajan (1964a)
f. Venkateswarlu *et al* (1959)
g. Venkateswarlu & Thanalakshmi (1962)
h. Nagarajan (1964b)
i. Radhakrishnan (1965)
j. Decius (1948)
k. Shimanouchi *et al* (1966)
l. Radhakrishnan (1964)
m. Thomas & Orville Thomaas (1972)
n. Miller & Carlson (1960)
o. Venkateswarlu & Sundaram (1955)
p. Haston & Claassen (1970)
q. Sathianadan (1962)
r. Stammreich *et al* (1956)

Table 2. Kinetic constants (10^{-23}g)

S. No.	Molecule	k_d	k_{dd}	k_α	$k'_{\alpha\alpha}$	$k'_{\alpha\alpha}$
1.	CF_4	2.4735	0.2270	0.1713	0.0040	−0.1605
2.	SiF_4	2.5788	0.1919	0.1888	−0.0136	−0.1357
3.	TiF_4	2.6709	0.1613	0.2042	−0.0289	−0.1140
4.	GeF_4	2.7512	0.1344	0.2176	−0.0423	−0.0951
5.	ZrF_4	2.7961	0.1195	0.2251	−0.0498	−0.0845
6.	PbF_4	2.9429	0.0706	0.2495	−0.0743	−0.0499
7.	CCl_4	4.5299	0.4522	0.3053	0.0217	−0.3198
8.	$SiCl_4$	4.6584	0.4095	0.3267	0.0003	−0.2895
9.	$TiCl_4$	4.7868	0.3667	0.3481	−0.0211	−0.2593
10.	$GeCl_4$	4.9135	0.3245	0.3692	−0.0422	−0.2294
11.	$ZrCl_4$	4.9913	0.2985	0.3822	−0.0551	−0.2111
12.	$SnCl_4$	5.0857	0.2671	0.3979	−0.0709	−0.1888
13.	$HfCl_4$	5.2353	0.2172	0.4229	−0.0958	−0.1536
14.	$PbCl_4$	5.2891	0.1993	0.4318	−0.1048	−0.1410
15.	CBr_4	10.0701	1.0659	0.6650	0.0722	−0.7535
16.	$SiBr_4$	10.2192	1.0154	0.6896	0.0475	−0.7187
17.	$TiBr_4$	10.3834	0.9615	0.7170	0.0201	−0.6799
18.	$GeBr_4$	10.5652	0.9011	0.7473	−0.0102	−0.6371
19.	$ZrBr_4$	10.6877	0.8601	0.7677	−0.0306	−0.6083
20.	$SnBr_4$	10.8492	0.8062	0.7947	−0.0575	−0.5701
21.	$HfBr_4$	11.1398	0.7094	0.8431	−0.1060	−0.5017
22.	$PbBr_4$	11.2560	0.6706	0.8624	−0.1253	−0.4744
23.	CI_4	15.9250	1.7153	1.0446	0.1260	−1.2129
24.	SiI_4	16.0792	1.6639	1.0703	0.1003	−1.1765
25.	TiI_4	16.2572	1.6044	1.1000	0.0706	−1.1345
26.	GeI_4	16.4621	1.5362	1.1341	0.0365	−1.0863
27.	ZrI_4	16.6047	1.4886	1.1580	0.0126	−1.0524
28.	SnI_4	16.8013	1.4230	1.1906	−0.0200	−1.0063
29.	HfI_4	17.1738	1.2989	1.2527	−0.0821	−0.9186
30.	PbI_4	17.3342	1.2454	1.2790	−0.1984	−0.8820

Table 3. Force constants (10 dynes cm^{-1})

S. No.	Molecule	f_d	f_{dd}	f_{α}	$f'_{\alpha\alpha}$	$f_{\alpha\alpha}$
1.	CF_4	8.0656	0.3931	0.2859	−0.1682	−0.2271
2.	SiF_4	6.7836	0.1283	0.0773	−0.0326	−0.0326
3.	TiF_4	5.0036	0.1826	0.0337	−0.0073	−0.0281
4.	GeF_4	5.5695	0.1880	0.0436	−0.0187	−0.0229
5.	ZrF_4	4.0651	0.1268	0.0256	−0.0096	−0.0108
6.	PbF_4	3.3280	0.0783	0.0264	−0.0109	−0.0057
7.	CCl_4	3.7769	0.2070	0.1389	−0.0842	−0.1116
8.	$SiCl_4$	3.3808	0.1256	0.0414	−0.0152	−0.0502
9.	$TiCl_4$	2.7960	0.1007	0.0219	−0.0052	−0.0191
10.	$GeCl_4$	2.8345	0.1533	0.0315	−0.0112	−0.0238
11.	$ZrCl_4$	2.6381	0.1373	0.0169	−0.0033	−0.0097
12.	$SnCl_4$	2.4759	0.1182	0.0201	−0.0085	−0.0115
13.	$HfCl_4$	2.4085	0.0361	0.0125	−0.0035	−0.0047
14.	$PbCl_4$	2.1116	0.0411	0.0129	−0.0035	−0.0043
15.	CBr_4	3.1268	0.0722	0.0543	−0.0154	−0.0886
16.	$SiBr_4$	2.8001	0.0403	0.0320	−0.0108	−0.0479
17.	$TiBr_4$	2.3474	0.0482	0.0174	−0.0031	−0.0200
18.	$GeBr_4$	2.3260	0.0845	0.0245	−0.0086	−0.0279
19.	$ZrBr_4$	2.2071	0.0522	0.0141	−0.0031	−0.0131
20.	$SnBr_4$	2.1226	0.0525	0.0113	−0.0006	−0.0079
21.	$HfBr_4$	1.7898	0.0633	0.0099	−0.0022	−0.0065
22.	$PbBr_4$	1.2503	0.0513	0.0085	−0.0028	−0.0072
23.	CI_4	2.2543	0.0387	0.0415	−0.0078	−0.0652
24.	SiI_4	2.1068	0.0016	0.0235	−0.0070	−0.0369
25	TiI_4	1.3424	0.1516	0.0250	−0.0115	−0.0403
26.	GeI_4	1.7935	0.0362	0.0200	−0.0050	−0.0247
27.	ZrI_4	1.3699	0.1197	0.0102	−0.0021	−0.0113
28.	SnI_4	1.5654	0.0319	0.0131	−0.0039	−0.0142
29.	HfI_4	1.3915	0.0390	0.0082	−0.0018	−0.0069
30.	PbI_4	1.2503	0.0513	0.0085	−0.0028	−0.0072

Table 4. Force constants in related molecules (10^5 dynes cm^{-1})

S. No.	Molecule	f_d	f_{dd}	f_α	$f'_{\alpha\alpha}$	$f'_{d\alpha}$
1.	CF_4	8.0656	0.3931	0.2859	—0.1682	—0.2271
2.	CCl_4	3.7769	0.2070	0.1389	—0.0842	—0.1116
3.	CBr_4	3.1268	0.0722	0.0543	—0.0154	—0.0886
4.	CI_4	2.2543	0.0387	0.0415	—0.0078	—0.0652
5.	SiF_4	6.7836	0.1283	0.0773	—0.0326	—0.0326
6.	$SiCl_4$	3.3808	0.1256	0.0414	—0.0152	—0.0502
7	$SiBr_4$	2.8001	0.0403	0.0320	—0.0108	—0.0479
8.	SiI_4	2.1068	0.0016	0.0235	—0.0070	—0.0369
9.	TiF_4	5.0036	0.1826	0.0337	—0.0073	—0.0281
10.	$TiCl_4$	2.7960	0.1007	0.0219	—0.0052	—0.0191
11.	$TiBr_4$	2.3474	0.0482	0.0174	—0.0031	—0.0200
12.	TiI_4	1.3424	0.1516	0.0250	—0.0115	—0.0403
13.	GeF_4	5.5695	0.1880	0.0436	—0.0187	—0.0229
14.	$GeCl_4$	2.8345	0.1533	0.0315	—0.0112	—0.0238
15.	$GeBr_4$	2.3260	0.0845	0.0245	—0.0086	—0.0279
16.	GeI_4	1.7935	0.0362	0.0200	—0.0050	—0.0247
17.	ZrF_4	4.0651	0.1268	0.0256	—0.0096	—0.0108
18.	$ZrCl_4$	2.6381	0.1373	0.0169	—0.0033	—0.0097
19.	$ZrBr_4$	2.2071	0.0522	0.0141	—0.0031	—0.0131
20.	ZrI_4	1.3699	0.1197	0.0102	—0.0021	—0.0113
21.	PbF_4	3.3280	0.0783	0.0264	—0.0109	—0.0057
22.	$PbCl_4$	2.1213	0.0379	0.0130	—0.0035	—0.0075
23	$PbBr_4$	1.7758	0.0809	0.0139	—0.0048	—0.0090
24.	PbI_4	1.2503	0.0513	0.0085	—0.0028	—0.0072
25.	$SnCl_4$	2.4759	0.1182	0.0201	—0.0085	—0.0115
26.	$SnBr_4$	2.1226	0.0525	0.0113	—0.0006	—0.0079
27.	SnI_4	1.5654	0.0319	0.0131	—0.0039	—0.0142
28.	$HfCl_4$	2.4085	0.0361	0.0125	—0.0035	—0.0047
29.	$HfBr_4$	1.7898	0.0633	0.0099	—0.0022	—0.0065
30.	HfI_4	1.3915	0.0390	0.0082	—0.0018	—0.0069

Table 5. Mean amplitudes (Å) at 298.16 K

S. N.	Molecule	$\sigma_d^{\frac{1}{2}}$	$\sigma_q^{\frac{1}{2}}$
1.	CF_4	0.0432	0.0539
2.	SiF_4	0.0392	0.0703
3.	TiF_4	0.0407	0.0959
4.	GeF_4	0.0386	0.0876
5.	ZrF_4	0.0420	0.1096
6.	PbF_4	0.0440	0.1108
7	CCl_4	0.0519	0.0672
8.	$SiCl_4$	0.0459	0.0868
9.	$TiCl_4$	0.0462	0.1130
10.	$GeCl_4$	0.0445	0.0946
11.	$ZrCl_4$	0.0457	0.1286
12.	$SnCl_4$	0.0465	0.1220
13.	$HfCl_4$	0.0464	0.1477
14.	$PbCl_4$	0.0489	0.1462
15.	CBr_4	0.0535	0.0747
16.	$SiBr_4$	0.0477	0.0945
17.	$TiBr_4$	0.0478	0.1235
18.	$GeBr_4$	0.0474	0.1074
19.	$ZrBr_4$	0.0472	0.1365
20.	$SnBr_4$	0.0482	0.1279
21.	$HfBr_4$	0.0525	0.1629
22.	$PbBr_4$	0.0510	0.1413
23.	CI_4	0.0597	0.0844
24.	SiI_4	0.0530	0.1091
25.	TiI_4	0.0682	0.1106
26.	GeI_4	0.0529	0.1175
27.	ZrI_4	0.0591	0.1596
28.	SnI_4	0.0546	0.1443
28.	SnI_4	0.0546	0.1443
29.	HfI_4	0.0567	0.1782
30.	PbF_4	0.0597	0.1772

First, the bond-angle interaction kinetic constants may be seen to possess mutually complementary roles such that their algebraic sum vanishes. Thus

$$k'_{d\alpha} + k''_{d\alpha} + k'_{d\beta} + k''_{d\beta} = 0$$

The second group of complementary kinetic constants relating to bending kinetic constants and angle-angle interaction kinetic constants behave such that their algebraic sum also vanishes on summation

$$k_{\alpha} + k'_{\alpha\alpha} + 4k''_{\alpha\alpha} + k_{\beta} + k'_{\beta\beta} + 4k''_{\beta\beta} + 2k_{\alpha\beta} + 2k'_{\alpha\beta} + 2k''_{\alpha\beta} = 0$$

The third group of kinetic constants involving stretching as well as bond-bond interaction kinetic constants, on summation, leads to the characteristic constant for any of the molecular type under study.

$$\Sigma k_d + \Sigma k_{dd} = 4 m_y$$

In addition to this general behaviour, the following characteristics may also be noticed in relation to the kinetic constants.

1. The kinetic constant $k'_{d\alpha}$ assumes the negative sign uniquely in all the cases.

2. The kinetic constant $k'_{\alpha\alpha}$ is positive or negative depending upon the molecule. In most of the cases, $k'_{\alpha\alpha}$ is negative while it is positive in a few cases.

3. In all the molecules, k_d , k_α and $k'_{d\alpha}$ increase when the mass of the X atom is increased. On the other hand, k_{dd} and $k'_{\alpha\alpha}$ exhibit decreasing trends.

3.2. Force Constants

Adopting the procedure followed in the earlier papers (Thirugnanasambandam *et al* 1969, 1974a b, 1975a-d, 1976a, b), the symmetry force constants of these molecules are evaluated. The individual force constants obtained from the symmetry force constants are given in table 3. From this table, it may be seen that the angle-angle interaction force constant $f'_{\alpha\alpha}$ and the bond-angle interaction force constant $f'_{d\alpha}$ are negative in all the cases studied here.

Table 4 deals with the force constants in related molecules. The major force viz., the stretching force constant f_d and the bending force constant f_α are naturally found to decrease with the decrease of electronegativity in the case of Y atoms. This observation is in line with the observations made with respect to planar and pyramidal XY_3 molecules in our earlier papers. (Thirugnanasabandam *et al* 1969, 1976a).

The high values of the stretching force constants in molecules having fluorine bonds may also be noticed, suggesting greater bond strengths in XF_4 molecules. (X = C,Si, Ti, Ge, Zr and Pb)

It is highly pleasing to note the occurrence of the same sign relating to the bond-angle interaction force constants as well as kinetic constants in all the molecules studied here. In most of the cases, the angle angle interaction force constants and the kinetic constants appear to have the same sign.

On the whole, it may be mentioned that the present values of the force constants are highly systematic and more reasonable than the earlier values available in the literature.

Comparing the present results with the values of the earlier investigators, it may be seen that the stretching force constant f_d agrees favourable with the values of earlier workers. With respect to f_{dd}, most of the present values are in good agreement with those of some of the authors. The bending force constant f_α and the interaction force constants $f'_{\alpha\alpha}$ and $f'_{d\alpha}$ appear to experience quite a considerable lowering in values as a consequence of the recognition of the reflex angle β.

3.3. Mean amplitudes

Using the symmetry force constant in the Cyvin's secular equation, the symmetrized mean square amplitudes have been obtained at the temperature 298.16 K. The values of the mean amplitudes of vibration for all the molecules have been computed from the symmetrized mean square amplitude values. These values, thus obtained in the present investigation, appear to be reasonable. It is highly interesting to note that the present values of the vibrational amplitudes compare favourably with the experimental values as also the calculated values, wherever such results are available (Cyvin 1968). The close agreements observed in all the cases studied here indicate that the present method of evaluating force constants are highly reasonable. As expected, the bonded mean amplitudes are in the increasing order from lower to higher members of the halogen series of Carbon, Silicon, Titanium, Germanium, Zirconium, Tin, Hafnium and Lead. This behaviour is opposite to that observed for the force constants in these cases. The present set of values will be useful in the interpretation of electron diffraction data relating to these molecules.

4. Conclusion

All the independent quadratic potential constants in thirty tetrahedral group IV halides have been redetermined here, introducing a new type of internal coordinates and hence a new set of symmetry coordinates. Wilson's F-G matrix method coupled with kinetic constants has been employed here in this investigation. The kinetic constants play a major role in the architecture of molecules and molecular dynamics. The force constants obtained by this new procedure seem to be highly reasonable and it may be mentioned that highly systematic sets of force constants are available here for the first time in these molecules. It is found that the mean amplitudes are related to kinetic constants in a significant manner. The mean amplitudes evaluated in the present study are in the expected range. The molecular constants, viz., the kinetic constants, the potential constants and the mean amplitudes studied in the present investigation appear to be highly interesting from the point of view of molecular dynamics. The extremely satisfactory results obtained here show that the Wilson's group theoretical techniques deserve to be applied in a stringent manner in any reasonable study of molecular vibrational problems.

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